THE TRUE ATOMIC WEIGHTS OF OXYGEN AND SILVER.

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(*Read December 2, 1910.*)

Chemists have been trying to determine the atomic weights of the chemical elements for now fully a century. Dalton introduced the idea in 1804, while Berzelius made the first reliable determinations as far back as 1814 and for a third of a century kept ahead of all others in this work.

While the laboratory work required for atomic weight determinations has been greatly improved since the time of Berzelius, the methods of reduction of the same by mathematical calculation have remained almost the same as those used by Berzelius a century ago. The work I have done in this line has hardly become known in this country, where the work done in one of the scientific departments at Washington, published by the Smithsonian Institution and disseminated under the official frank, continues to be upheld as the standard through the Committee on Atomic Weights of the American Chemical Society. But at the opening of the volume for the present year it is declared that "there is confusion and uncertainty throughout the table of atomic weights."[1]

It therefore seems desirable that this question be considered independent of the dominant chemical school by those who, like electricians and physicists, come in contact with the broad question of the constitution of matter which involves that of the atomic weights of the chemical elements.

In the old Berzelian calculations the atomic weight of oxygen is assumed as a fixed constant (100 by Berzelius, 16 at present) and all other atomic weights are referred to this standard. This system has led to the now "official" value 107.88 for silver, a value which I have repeatedly shown to be in conflict with the most renowned

[1] *Journal Am. Chem. Soc.*, 1910, p. 4.

recent determinations to the extent of over one tenth of one per cent.

This is not the place for renewing the discussion in detail; the publications in question are accessible to all. We would rather take up the question in the broadest way and try to decide it by a sort of crucial test. *We will show that the evidence on which the value 16 for oxygen rests is exactly the same as that which gives the value 108 for silver.*

It is a fact that all chemical reactions are approximately exact only and that all laboratory work is subject to the same limitation. It is therefore incorrect to assume that in the reactions and in the laboratory work there is involved no error whatever on the part of the oxygen and that all errors are due to the other elements associated with oxygen. It seems sufficient to state this to have it admitted.

But if oxygen be supposed free from all material imperfections, as is assumed in the common calculations, its actual shortcomings are not blotted out thereby—they are simply placed to the account of the other elements which are unfortunate enough to be in reaction with the supposedly perfect element, assumed to be immune from error by the school. Hence the errors of the associated elements will be correspondingly magnified. In this way, the dominant school now has arrived at the value 107.88 for silver.

Let us try to see how this has been brought about and how the question may be put in the above crucial form for decision.

It is agreed by all and not even denied by the American School that the atomic weight, for $O = 16$, is very near the round numbers: Ag 108, Cl 35.5, C 12, N 14, etc. These values we have called the *absolute atomic weights.*

Accordingly, the *true atomic weights* can differ from these absolute values by small fractions only; this we call the *departure* and designate by the letter epsilon (ϵ).

Hence the real mathematical problem is the *determination of the departure for each element in every reaction used.* We determine the departure in thousandths of the unit. Thus, if the American Chemical School be right in declaring that the atomic weight of silver is 107.88, the departure for silver would have the enormous value

— 120, while for the element oxygen in all reactions and in all determinations made by all chemists at all times and under all conditions the departure was zero always.

But is this introduction of the departure for the entire atomic weight not merely a formal matter? Not to the man versed in higher mathematics; for he knows that even the most complex functions permit a simple solution by proportional parts for all cases in which the increment of the variable is sufficiently small. Thus this solution would even hold true, with fair approximation, for the departure of 120 thousandths of a unit, above indicated. We may therefore express the difference between the Berzelian reduction maintained to the present day by the dominant school of chemistry and our own as corresponding to the difference between common algebra and higher mathematics.

While we have worked with the departures instead of the entire atomic weight for over twenty years, we had not been able to determine the relation between the different departures of the different elements in a given chemical reaction until we discovered the equation of condition in 1907. Since then we have determined the departures for each element in all the three hundred chemical reactions that have been used for the determination of atomic weights during the entire century. The results have been put into five tables, each giving sixty reactions. The first two of these tables have been published, the other three have been ready for publication since the close of 1909.

Now we may return to the point at issue, the value of the atomic weight of silver: is it 107.88 or is it 108, on the scale of 16 for oxygen?

Our tables show that oxygen occurs in 158 of the reactions used for the determination of atomic weights, while silver occurs 115 times. Consequently the atomic weight of oxygen has been determined 158 times and that of silver 115 times. Of course, the dominant school will declare that they have done no such thing; but that will not prevent us from using the data they have published although we will accept their declaration as made in good faith.

The following table gives the results obtained, as stated repeat-

edly: departures (expressed in thousandths of the unit) from the absolute values 16 and 108.

TABLE OF DEPARTURES ϵ (IN THOUSANDTHS).

Departures.	0–10	11–20	21–100	0–20	21–40	41–100	0–100	101–
OXYGEN.								
No. of cases	89	30	33	119	17	16	152	6
Mean ε	1	5	—1	2	14	—17	1	
SILVER.								
No. of cases	39	22	36	61	22	14	97	18
Mean ε	—1	—5	—23	—2	—5	—54	—10	
No. per cent.								
Oxygen	58	20	22	78	11	11	100	4
Silver	40	23	37	63	23	14	100	18
Mean	49	21	30	70	17	13	100	—
All 656								
Determ. for all elements	49	21	30	70	18	12	100	7

An extended study of this table would be most instructive, but a brief summary must answer here.

It is noted that we have given two distinct sets of returns: by intervals of 10 and of 20 thousandths of the departure. In each set we have given only the first two intervals, putting all the others into a third column. The table itself shows the reason for these modes of record in *the great predominance of the small departures.*

This very predominance of the small departures means that the real departures are minute and the actual departures here tabulated as the results of the experimental work done during the century prove the absolute atomic weights to be the real atomic weights of nature. The question of a minute weight of the chemical valence, touched upon in our recent publications, does not come under consideration here.

The table shows that 50 per cent. of all cases give departures below 10 thousandths (0.01) and 70 per cent. below 20 thousandths (0.02) on all the 656 atomic weight determinations made by all the 300 reactions employed. This proves that the determinations have for their limit the absolute atomic weights themselves and that the departures represent mainly the imperfections of the experimental work.

The relatively few larger departures (only about 12 per cent.)

above 40 thousandths (0.04) are mainly due to the fact that we have taken all reactions used without excluding those known to be imperfect and which are generally excluded by others.

It will also be noticed that the mean departure for the greatest number of cases is only one or a few thousandths; it is without significance in the question here considered.

This question can now be fully answered. Bearing in mind that increased atomic weight necessarily brings a slight increase in the departures for experimental reasons, we must admit that *the departures for oxygen and for silver are essentially alike, so that the values $O = 16$ and $Ag = 108$ stand and fall together.* If oxygen is 16, then silver is 108, with nearly the same degree of precision. Again, if the value 108 is denied for silver, then the value 16 for oxygen is equally untenable.

Finally, it appears to me that it has been fully demonstrated that the assumption of immunity from error for oxygen is as false in fact as it is absurd in philosophy; possibly that accounts for the tenacity with which the school has clung to the same.

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